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MANUFACTURE OF FURFURAL PRACTICABLE IN HUNGARY

Dr Lorant Borsodi

Procurement of sufficient domestic raw materials is the major problem of Hungarian industry. Many basic materials may be produced from by-products which have never been utilized up to now. Furfural is such a material, and it may be manufactured from wood and agricultural scrap.

Furfural has been known for a long time and many uses for it have been worked out, but later discontinued. Today, furfural is in the foreground again.

Furfural and its derivatives are used in the manufacture of many industrial materials, substitutes, solvents, and drugs. It is used in the synthetics, leather, and rubber industries.

Manufacture

There are two processes for the preparation of furfural:

1. It can be obtained as a by-product in processes involving cellulose, which contains vegetable matter.

2. It may be the end-product, in processes utilizing vegetable matter.

Czechoslovak experience indicates that furfural may be prepared by hydrolyzing solutions containing large quantities of pentosans, which are formed during the processing of cane and straw cellulose.

The cane cellulose of the Petohaz sugar plant would be suitable for this purpose, and 100-150 tons of furfural could be obtained yearly.

The manufacture of straw cellulose is being carried on on a much larger scale, but more complicated processes are required to utilize the by-products of this method.

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The other possibility would require basic changes in certain phases of the agricultural industry.

In agricultural alcohol production, inferior corn and potatoes are utilized and molasses is fermented. The available supply of these materials will decrease during the Five-Year Plan because of the development of agriculture and the use of synthetic ion-exchange resins in the sugar industry. The agricultural alcohol industry is, therefore, forced to search for new raw materials: straw, potato stalks, sunflower-seed husks, and wood scrap. Abroad, many kinds of sugar are prepared by the acid hydrolysis of these products, which shows that the materials are quite suitable for fermentation. Furfural is obtained as a by-product of the hydrolysis of cellulose.

If furfural is desired as an end-product, the process for the extraction of furfural from sunflower-seed husks must be used. Sunflower-seed husks contain 30 percent pentosan and 40 percent cellulose, from which 14-15 percent furfural may be obtained.

The process involving sunflower-seed husks takes place in a rotary drum, made of steel and lined with copper. It is 4 meters long and 1.5 meters in diameter. Under a pressure of 4-5 atmospheres, the husks are moistened with 5-6 percent sulfuric acid, and steam under 4-5 atmospheres is forced through the chamber. The drum revolves at 4 revolutions per minute. The mixture of furfural and steam is led into a condensation chamber. The mixture then goes into a copper fractionating column, 8 meters tall, having 30 plates. The product which emerges from the fractionating column contains 50-55 percent furfural. With vacuum distillation, 99 percent furfural can be obtained.

It is not economical to run a plant solely for the manufacture of furfural. The manufacture of furfural in small quantities involves high costs. Two 40-meter rotary drums are necessary to produce 2 tons daily. The necessary machinery would cost 500,000 forints, and the building an additional 500,000 forints.

Thanks to this process, furfural was manufactured during 1945-1946, with primitive equipment. Experiments were carried out to determine to what extent the speed-up of the pentosan hydrolysis was dependent on the temperature and concentration of the acid. The quantity of steam necessary for preparing one ton of furfural was determined. With more modern methods, the quantity required may be reduced by about 50 percent.

Uses

Furfural is used as a raw material for the production of synthetic substances, as a solvent, as a preservative and disinfectant, as a raw material for the chemical industry, and for miscellaneous uses.

1. Production of Synthetic Substances

Among the polycondensation resins, the phenol-formaldehyde and carbamide-formaldehyde resins are the best known. The application of furfural to replace formaldehyde in case of the bakelite resins has now been worked out. In many cases, the furfural resins have proved to be superior. They are heat resistant, they are good insulators, and they resist corrosion. Their disadvantage is that colorless or light-colored resins cannot be obtained if they are used.

While 96 kilograms of furfural and 94 kilograms of phenol reacted to form 172 kilograms of resins, 80 kilograms of formaldehyde and 94 kilograms of phenol yielded 106 kilograms of resins. This means that, in the case of the first reaction, 18 kilograms of water and in the case of the second, 68 kilograms of water, were liberated. Another advantage in the case of the furfural

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resins is that the mixing and the hexamethylenetetramine hardening can be accomplished in one step. The furfural resins are liquids and remain easy to mold until they are hardened by heat.

The formaldehyde resins reach the solid state by going through a rubberlike stage.

Furfural resins harden between 165 and 182 degrees. Under 165 degrees, they are easy to pour into molds, and thus are especially suitable for application to the bakelite-sprinkling process.

The formaldehyde resins harden at only 149 degrees.

The phenol-furfural resins have wide application. In certain fields, they are used exclusively. They are used as binders in the carbon brushes of electric motors and for pasting electric lamps to their bases. They are used in the impregnation of glass fibers and in the manufacture of materials resistant to chemical corrosion. The diluted furfural solution penetrates pores easily and reduces porosity, thereby increasing the mechanical resistance of porous materials.

A special use of furfural resins is their application in the manufacture of light-sensitive resins, used in photochemistry, photolithography, and color photography. They are products of furfural and various ketones. They are soluble in benzene, but become insoluble on contact with light.

The resin-type compound of lignin with furfural is suitable for the manufacture of construction materials. To provide all the furfural that could be utilized in this field, most agricultural scrap would have to be used for the manufacture of furfural.

Phthalic anhydride is used as the starting material for alkyd-type synthetic resins, which are used in the lacquer industry. Adipic acid can easily be substituted for phthalic anhydride. Adipic acid is prepared by oxidizing tetrahydrofurfural, and adipic acid is the starting material for synthetic fibers and nylon-type materials.

Another type of furfural resin is obtained through the polycondensation of furfuryl alcohol. Furfuryl alcohol is prepared by hydrogenating liquid furfural. Upon the action of temperature and acid, furfuryl alcohol becomes resin.

Beginning in 1953, 1,000 tons of formaldehyde can be saved yearly through the use of furfural. This would eliminate the use of methyl alcohol, which is necessary in the preparation of formaldehyde.

With the additional use of furfural in synthetic-resin manufacture, it will be possible to obviate the import of 4,000 to 5,000 tons of phthalic anhydride, or the imported naphthalene from which the required quantity of phthalic anhydride is produced. Thus, the basis for the synthetic-fiber industry, envisaged in the second Five-Year Plan, could be laid.

2 Solvent

Furfural is especially effective in the purification of lubricating oils, of basic synthetic-rubber ingredients, and of vegetable oils, since it dissolves naphthenes, sulfur compounds, and other undesirable components. Purification of oils with furfural removes unstable hydrocarbons which form a sludge harmful to cylinders and pistons. It also improves the viscosity index of oils, so that the oils render good service at both low and high temperatures. This is an especially important factor in the case of diesel oils, where the combustion temperature plays such an important role.

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Furfural is nontoxic and does not corrode metals. It is possible to refine it at 80 - 100 degrees centigrade, which is a suitable temperature for the extraction of paraffin oils. Furfural is suitable for the purification of both the distillate and the residue and increases the yield by 10 percent compared to other solvents.

The solvent, furfural, is indispensable in Hungarian lubrication-oil production. For a yearly output of 10,000 tons of heavy oils, 1,000 tons of furfural are necessary to start production. Since the production of 5,000 tons of quality lubricating oils is planned, 1,000 tons of furfural will be required to replace losses.

a. Synthetic-rubber Industry

A synthetic-rubber plant is to be built during the second Five-Year Plan. The basic material in synthetic-rubber production is butadiene. The cheapest source of butadiene is the butane found in natural gas, as well as the butane contained in the by-products of the cracking process.

With the aid of furfural, the boiling point of the gas mixture is changed so that 100-percent pure butadiene can be obtained. In this case, furfural containing 4-5 percent water is used, because water greatly stimulates the selectivity of the solvent. An advantage of the process is that the furfural is easy to separate from the polymerized acid particles, and not more than 1-2 percent of the circulating solvent needs to be purified.

b. Purification of Vegetable Oils

One of the most important problems of the lacquer industry is the procurement of drying oils. Linseed oil must be imported. With the aid of furfural, the drying portion can be extracted from vegetable oils, and the residue is very suitable for the manufacture of edible oils. Soybean oil especially lends itself to this extracting process.

c. Purification of Tall Oil

During the preparation of cellulose sulfate, so-called tall oil is formed. This oil, which is used in soap manufacture, is well known for its foul odor. The cheapest solvent used to eliminate this odor is furfural.

d. Purification of Wood Resin

Both the paper and soap industries require a pure, light-colored resin which is not only expensive, but difficult to obtain.

Resins contain two kinds of pigments. One lends a ruby tint to the resin and may be removed by steam distillation. The other is red and cannot be removed by steam distillation. A red dye is obtained when lye is added, and furfural removes this dye.

The resin is dissolved in benzene and treated with furfural. The two solutions, one containing furfural and the other benzene, separate sharply when cold. Thus, both the pure resin and the dye can be removed, with a minimum loss of solvents.

e. Application of Furfural in the Dye Industry

Furfural and furfuryl alcohol are excellent high-boiling-point solvents, used in the dye industry as lacquer solvents and paint removers. Furfural and its derivatives greatly resist oxidation and are water repellent.

Furfural and its derivatives are very useful in dissolving such insoluble synthetic materials as cellulose esters, vinyl derivatives, phenol resins, and aromatic substances.

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3. Preservative and Disinfectant

In general, furfural is a preservative and a disinfectant. It is used, therefore, as a germicide, weed killer, and a protective material for plants and trees. Furfural prevents disease in cereals and the development of bacteria and molds.

Furfural has the capacity to penetrate very deeply. It is very useful, therefore, in wood impregnation and thorough weed-killing. It is more effective than formaldehyde. Swimming pools can be disinfected with very small quantities of furfural. A one-percent water solution of furfural kills parasites on the human body and all microorganisms which adhere to its surface.

Furfural is also more effective than formaldehyde in combating poultry lice and in washing coops for the prevention of poultry diseases.

4. Furfural as a Raw Chemical

Furfural and its derivatives, especially the esters and ethers of tetrahydrofurfuryl alcohol, are excellent softeners.

The basic materials of many organic dyes are furan-type compounds. Malachite green, brown, and yellow dyes may be prepared from furfural. It reduces the costs of production.

Furfural is used in important compounds in the rubber industry to accelerate vulcanization and to retard oxidation. The rubber industry utilizes so-called anticreasing products which increase the elasticity of rubber.

The textile industry uses furfural as a humidifying agent. Furfural is useful to the automobile and airplane industries. It is used (as a fuel additive?) to absorb hydrocarbons and prevents them from settling on the walls of the cylinders in the form of carbon and oil.

5. Miscellaneous Uses

Because of its humidifying properties, furfural is used in the subsurface construction industry. It is used widely in road construction. By effecting a thorough mixing of bituminous and mineral matter, it brings about better adhesion.

When furfural is used as a humidifying agent and is subjected to heat, a resin is formed which greatly increases the resistance of the pavement to weather. Cracking stops because the resins are water resistant. Furfural lengthens the life span of roads by about 15-20 percent.

Also, because of its humidifying properties, furfural is utilized in the manufacture of abrasives. The addition of furfural makes these products much more durable. The increased durability is due to the action of the resins which are formed by heat.

Comment on Dr Borsodi's Article by Dr Jozsef Marton

"Dr Borsodi is somewhat optimistic, though the possibilities are great. It would take more than one million forints, in my opinion, to build a furfural plant with a 1,000-ton yearly output. Costs could be reduced greatly if the existing sugar refineries could be utilized and equipped with the necessary additional equipment."

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